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Calculations of Zn II $3d^9 4s5s$ and Ag I $4d^9 5s6s$, and Some New Levels in these Spectra

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Results of intermediate-coupling calculations are given for Zn II $3d^9 4s5s$ and Ag I $4d^9 5s6s$. A $[(4d^9)J_I, (5s6s)J_{II}]J$ coupling scheme is appropriate for the latter. New $3d^9 4s(^3D)5s\ ^2D_{2\frac{1}{2}}$ and $3d^9 4s(^1D)5s\ ^2D_{2\frac{1}{2}}$ levels were found in Zn II, and a few other additions and revisions are given for the analysis. The combinations of the new levels $3d^9(^2D)4s4p(^3P^\circ)\ ^4F^\circ_{4\frac{1}{2}}$ in Zn II and $4d^9(^2D)5s5p(^3P^\circ)\ ^2F^\circ_{2\frac{1}{2}}$ in Ag I are also listed.

Key words: Atomic spectra; energy levels; silver; zinc.

1. Introduction

A recent fitting of some d^9sp configurations to intermediate coupling theory provided useful comparisons of experimental with predicted levels in several spectra [1].[1] We also made similar calculations for Zn II $3d^9 4s5s$ and Ag I $4d^9 5s6s$. The results of these d^9ss calculations are reported here, along with the supporting combinations for a few new or revised level positions found during the course of the d^9sp and d^9ss work. Some new wavelength measurements for Zn II in the vacuum ultraviolet, and redetermined energy level positions based partially on these measurements, are given in an accompanying paper [2].

2. Zn II

Our first few energy-matrix diagonalization and level-fitting iterations [1] for Zn II $3d^9 4s4p$ indicated that the position previously listed [3] for $^4F^\circ_{4\frac{1}{2}}$ was incorrect. A search with Dick's [4] line list yielded the new level and combinations for $^4F^\circ_{4\frac{1}{2}}$ shown in table 1. The line at 54538.3 cm^{-1} arising from $4p'\ ^4F^\circ_{4\frac{1}{2}} - 5s'\ ^4D_{3\frac{1}{2}}$ was apparently not resolved on Dick's plates from a line at 54541.1 cm^{-1} ($4s^2\ ^2D_{2\frac{1}{2}} - 4f\ ^2F^\circ$). The quoted wavenumbers are from new observations [2] where the two lines are well resolved and show different excitation characteristics, each proper for the assigned classification.

The $3d^9 4s(^3D)5s\ ^2D_{2\frac{1}{2}}$ level at 164998.9 cm^{-1} in table 1 also replaces a previous level that did not fit the calculation. The results of fitting intermediate coupling theory[2] to Zn II $3d^9 4s5s$ are given in tables 2 and 3. The five parameter values in table 3 are determined by only seven known levels. It is seen, however, that these values scale well with the corresponding values[3] for Cu I $3d^9 4s5s$ where all eight levels are known. A check on the value of $G_2(3d, 4s)$ for Zn II is given by the fact that it is only slightly less that the value 1914 cm^{-1} for Zn III $3d^9 4s$. The presence of the $5s$ electron has little effect on the $3d$–$4s$ interaction, in agreement with a similar comparison of these two configurations in Cu I and Cu II, respectively.

The $3d^9 4s(^1D)5s\ ^2D_{2\frac{1}{2}}$ level in table 2 was also found by searching near the position predicted in earlier diagonalizations. Some combinations of this new level are given in table 1.

[1] Figures in brackets indicate the literature references at the end of this paper.

[2] The d^9ss energy matrices were calculated independently for this work. They include an additive constant A, related to the configuration center of gravity (c.g.) as follows:

$$A = (\text{c.g.}) + \tfrac{1}{2}[G_2(ds) + G'_2(ds) + G_0(ss)].$$

A description of the procedure for least-squares fitting of level positions to obtain energy parameter values is given by Racah [5]. We use the term "rms error" to describe the level fits. This is defined as

$$\left[\left(\sum_{i=1}^{N} \delta_i^2\right)/(N-M)\right]^{1/2},$$

where δ is the difference between the experimental and calculated level positions, N is the number of experimental levels entered into the fitting procedure, and M is the number of free parameters.

[3] Our fitted values for the Cu I parameters are in agreement with those recently published by Wilson [6].

TABLE 1. *Combinations of some* Zn II *levels*

All but four of these levels were given by Crooker and Dick [3]. The positions have been redetermined, partly on the basis of new observations [2]. Wavenumbers of lines with intensities in parentheses are from [2], and the others are from [4].

			$3d^9 4s(^3D)5s$		$(^1D)5s$	$3d^9 4s4d$?			$3d^9 4s(^3D)6s$	
			$^4D_{3\frac{1}{2}}$	$^2D_{2\frac{1}{2}}$	$^2D_{2\frac{1}{2}}$	$1_{3\frac{1}{2}}$	$7_{3\frac{1}{2}}$	$12_{3\frac{1}{2}}$	$21_{4\frac{1}{2}}$	$^4D_{3\frac{1}{2}}$
			161318.4	164998.9[a]	167624.4[a]	169150.5[b]	171643.0[b]	173003.1	173561.9[a]	191198.
$3d^9(^2D)4s4p(^3P^\circ)$	$^4P^\circ_{2\frac{1}{2}}$	103701.6	(80) 57616.7	20 [c]61298.4	6 63923.5	(100) 65448.7	(50) 67941.2	5 69301.9		1 87496.4
	$^4F^\circ_{4\frac{1}{2}}$	[a]106779.9	(150) 54538.3			(100) 62370.8	(40) 64863.2	5 66223.2	(80) 66782.0	8 84421.8
	$^4F^\circ_{3\frac{1}{2}}$	106852.4	(40) 54466.0			8 62297.7	(40) 64790.8	(12) 66151.0	(30) 66708.8	1 84344.8
	$^4F^\circ_{2\frac{1}{2}}$	107268.6	10 54050.0			3 61883.1		(40) 65734.3		
	$^2F^\circ_{2\frac{1}{2}}$	110672.3	12 50646.6		10 56952.6	10 58477.8		15 62330.7		0 80523.5
	$^4D^\circ_{3\frac{1}{2}}$	110867.2	(50) 50451.3			60(5) 58283.2	(60) 60776.0	25 62135.3	(100) 62694.9	2 80331.1
	$^4D^\circ_{2\frac{1}{2}}$	111743.0	25 49576.1		8 55881.3	18 57407.6	2 59899.9	15 61259.9		00 79454.6
	$^2F^\circ_{3\frac{1}{2}}$	112409.7	30 48909.6	60 52589.4	(15) [d]55214.9	25 56741.0	15 59233.3		20 61151.7	
	$^2P^\circ_{1\frac{1}{2}}$	113499.2			75 54125.4					
	$^2D^\circ_{1\frac{1}{2}}$	114045.0			10 53580.1					
	$^2D^\circ_{2\frac{1}{2}}$	114833.9	10 46485.3	50 50166.4	75 52791.1			2 58168.8		1 76363.8
$3d^9(^2D)4s4p(^1P^\circ)$	$^2F^\circ_{3\frac{1}{2}}$	130014.3		50W 34984.3	[e]30 37609.0					
	$^2D^\circ_{2\frac{1}{2}}$	131650.9		100W 33348	15 35973					
	$^2F^\circ_{2\frac{1}{2}}$	133145.8		30W 31851	30 34480					

[a] New level.
[b] J-value of level changed here.
[c] Line also classified by another transition [3].
[d] Line newly resolved from stronger neighboring line [2].
[e] Line also classified by Zn III transition [4].

TABLE 2. *Calculated energy levels for* Zn II $3d^9 4s5s$

The last column gives the percentage of the leading eigenvector component in the scheme of the first column.

Term	J	Experimental cm^{-1}	Calculated cm^{-1}	E–C cm^{-1}	LS %
$3d^9 4s(^3D)5s\ ^4D$	$3\frac{1}{2}$	161318	161322	−4	100
	$2\frac{1}{2}$	162070	162068	2	85
	$1\frac{1}{2}$	162897	162892	5	74
	$0\frac{1}{2}$	164070	164070	0	100
$(^3D)5s\ ^2D$	$2\frac{1}{2}$	164999	164999	0	88
	$1\frac{1}{2}$	165277	165279	−2	46
$(^1D)5s\ ^2D$	$2\frac{1}{2}$	167624	167624	0	92
	$1\frac{1}{2}$		169268		57

TABLE 3. *Energy parameter values for three* d^9msns *configurations*

Unit is cm^{-1}

	Zn II $3d^9 4s5s$	Cu I $3d^9 4s5s$	Ag I $4d^9 5s6s$
A	166409.6 ± 4	65964.3 ± 3	84199.3 ± 20
$G_2(d, ms)$	1884.8 ± 4	1550.0 ± 3	1874 ± 102
$G_2'(d, ns)$	291.4 ± 4	158.9 ± 3	197.5 ± 27
$G_0(ms, ns)$	1812.0 ± 6	1021.9 ± 3	886 ± 19
ζ_d	1099.1 ± 3	826.0 ± 2	1818 ± 10
rms error[2]	5	4	25

3. Ag I

The $4d^9 5s6s$ configuration in this atom begins 18306 cm^{-1} above the Ag II ($4d^{10}\ ^1S$) limit. The levels having $J = 1\frac{1}{2}$ or $2\frac{1}{2}$ are thus broadened by autoionization into the $4d^{10}\epsilon d\ ^2D$ continuum. This mixing with the continuum may help account for the larger standard errors on the parameter values we obtained for Ag I $4d^9 5s6s$ (table 3). The same seven levels are known experimentally as for Zn II, but the level rms error is 25 cm^{-1} for Ag I. The value for the Ag I parameter with the largest standard error, $G_2(4d, 5s) = 1874 \pm 102$ cm^{-1}, compares well with the Ag II value 1942 cm^{-1} obtained directly from the experimental levels of $4d^9 5s$. Both values may be affected by neglect of configuration interaction, since the Ag II value for G_2 given by a general treatment [7] of $(4d+5s)^n$ is 2045 ± 17 cm^{-1}.

The calculated levels are given in table 4. On inspection of the experimental levels, we noticed that whereas the $4d^9 5s(^3D)6s\ ^2D$ and ^4D terms overlap badly, the levels appeared to fall into separated terms based on the coupling scheme $[(d^9)J_I, (ss)J_{II}]J$. As may be seen in table 4, the latter scheme is indeed more appropriate than LS coupling. The $J_I J_{II}$ percentage compositions were obtained by a transformation from the $(d^9)s$ LS scheme of our matrices.[4] For those six levels having coupling-dependent purity, the average purity in $J_I J_{II}$ coupling is 82 percent, as compared with 62 percent in the LS scheme.

TABLE 4. *Calculated energy levels for* Ag I $4d^9 5s6s$

The largest component in each of the two coupling schemes is given for each level.

Name $[(4d^9)J_I, (5s6s)J_{II}]$	J	Experimental cm^{-1}	Calculated cm^{-1}	E–C cm^{-1}	$J_I J_{II}$ %	Term	LS %
$[2\frac{1}{2}, 1]$	$3\frac{1}{2}$	79413	79424	−11	100	$4d^9 5s(^3D)6s\ ^4D$	100
	$2\frac{1}{2}$	80164	80175	−11	84	^4D	65
	$1\frac{1}{2}$	81266	81242	24	87	^4D	48
$[2\frac{1}{2}, 0]$	$2\frac{1}{2}$	82070	82066	4	79	$4d^9 5s(^3D)6s\ ^2D$	68
$[1\frac{1}{2}, 1]$	$0\frac{1}{2}$	83983	83969	14	100	$4d^9 5s(^3D)6s\ ^4D$	100
	$1\frac{1}{2}$	84594	84606	−12	79	$^4D^a$	49
	$2\frac{1}{2}$	86484	86490	−6	82	$4d^9 5s(^1D)6s\ ^2D$	81
$[1\frac{1}{2}, 0]$	$1\frac{1}{2}$		87429		81	$4d^9 5s(^1D)6s\ ^2D$	64

[a] The LS name for this level would be $(^3D)^2D$, which comprises 41 percent of the calculated composition.

The $J_I J_{II}$ term structure of this configuration is apparent in figure 1. There is no overlapping of the four terms, and the largest of the interactions contributing to the structure, the $4d^9$ spin-orbit interval $2\frac{1}{2}\ \zeta_d$, is nicely exhibited.

As a result of our calculations [1] *for Ag* I $4d^9 5s5p$ we found a new level $4d^9(^2D)5s5p(^3P^\circ)\ ^2F^\circ_{2\frac{1}{2}}$ (designated $5p'\ ^2F^\circ_{2\frac{1}{2}}$). Five combinations are given in table 5 for this level, three of the lines not having been previously classified [8]. The character of these lines shows the level to be wide, as expected because of autoionization. The circumstance that its strongest expected transition, to $4d^9 5s^2\ ^2D_{1\frac{1}{2}}$, is masked by the much stronger resonance line at 3382.89 Å probably explains previous failure to find this level. Some other results of the $4d^9 5s5p$ work as it affected line classifications are also given in table 5. The levels of $4d^9 5s6s$ are given LS names in this table to make it consistent with Shenstone's full line list.

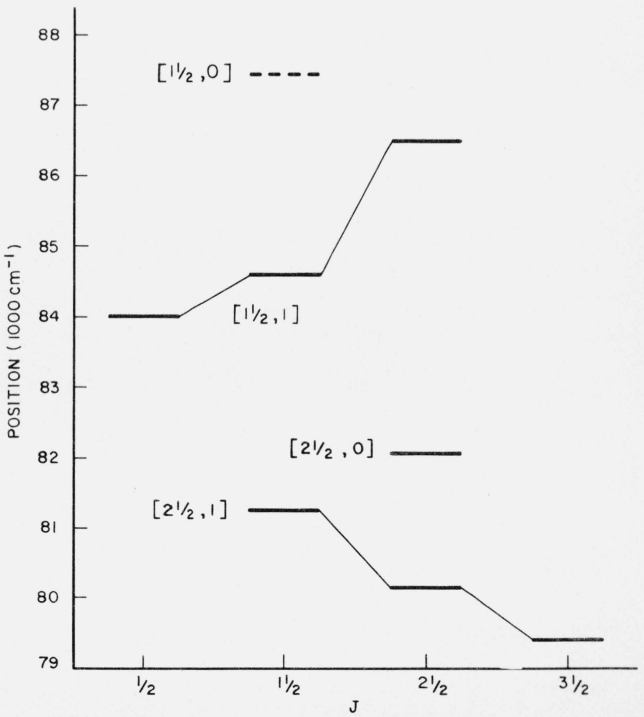

FIGURE 1. *Energy levels of* Ag I $4d^9 5s6s$.

The connected levels form terms in the $[(4d^9)J_I, (5s6s)J_{II}]J$ coupling scheme appropriate for this configuration. The $[1\frac{1}{2}, 0]$ level has not been observed.

[4] This transformation was actually accomplished by first diagonalizing the matrices with all parameters zero except ζ_d and G_0 (ss). See [5].

TABLE 5. *Classifications of some* Ag I *lines*

Wavelengths and intensities are from Shenstone [8]. Configurations and parentages for the levels are indicated by use of the designation scheme of AEL [8]. Notes:

A. Name of the $4d^9 5s5p$ level involved in transition was changed in [1].
B. Line was previously listed as doubly classified, with one of the transitions belonging to the now rejected level at 62934 cm^{-1}
C. New classification.

λ(air) Å	Int.[a]	σ(vac) cm^{-1}	Classification	Note
6010.1	5U	16634.	$5p'\ ^2D^\circ_{1\frac{1}{2}} - 6s'\ ^4D_{2\frac{1}{2}}$	A
5801.92	5U	17230.9	$5p'\ ^4D^\circ_{2\frac{1}{2}} - 6s'\ ^4D_{3\frac{1}{2}}$?[b]	B
5637.01	5U	17735.0	$5p'\ ^2D^\circ_{1\frac{1}{2}} - 6s'\ ^4D_{1\frac{1}{2}}$	A
4917.5	10UU	20330.	$5p'\ ^2F^\circ_{2\frac{1}{2}} - 6s'\ ^2D_{1\frac{1}{2}}$	C
4888.21	20	20451.7	$5p'\ ^2D^\circ_{1\frac{1}{2}} - 6s'\ ^4D_{\frac{1}{2}}$	A
4745.93	2U	21064.8	$5p'\ ^2D^\circ_{1\frac{1}{2}} - 6s'\ ^2D_{1\frac{1}{2}}$	A
4615.69	30U	21659.2	$5p'\ ^4P^\circ_{1\frac{1}{2}} - 6s'\ ^4D_{2\frac{1}{2}}$	B
4499.50	1U	22218.5	$5p'\ ^2F^\circ_{2\frac{1}{2}} - 6s''\ ^2D_{2\frac{1}{2}}$	C
4354.7	5UU	22957.	$5p'\ ^2F^\circ_{3\frac{1}{2}} - 17$ $5p'\ ^2F^\circ_{2\frac{1}{2}} - 14_{2\frac{1}{2}}$	C
3542.608	50	28219.76	$5p'\ ^4F^\circ_{4\frac{1}{2}} - 12$?[b]	B
3469.16	30	28817.2	$5s^2\ ^2D_{1\frac{1}{2}} - 5p'\ ^2D^\circ_{1\frac{1}{2}}$	A
3382.893	1000R	29552.04	$5s\ ^2S_{\frac{1}{2}} - 5p\ ^2P^\circ_{\frac{1}{2}}$ $5s^2\ ^2D_{1\frac{1}{2}} - 5p'\ ^2F^\circ_{2\frac{1}{2}}$	C
2938.42	20U	34022.	$5s^2\ ^2D_{2\frac{1}{2}} - 5p'\ ^2F^\circ_{2\frac{1}{2}}$	C
λ(vac)				
1574.02	5	63531.6	$5s\ ^2S_{\frac{1}{2}} - 5p'\ ^2D^\circ_{1\frac{1}{2}}$	A
1507.37	50RUU	66341.	$5s\ ^2S_{\frac{1}{2}} - 5p'\ ^4D^\circ_{1\frac{1}{2}}$	A

[a] The letter "U" was used in [8] for wide lines (German *unscharf*).

[b] Classification given as questionable by Shenstone [8]' The strong line at 3542.6 Å does not have the wide character expected for transitions from the autoionizing $5p'\ ^2F^\circ_{2\frac{1}{2}}$ level. No classification has been found for this line except that given. (The three combinations of the even level 12 of Shenstone were given with question marks, so presumably the level itself was considered doubtful.)

4. References

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